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REACTIVE WETTING OF LIQUID METALS ON CERAMIC SUBSTRATES

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Abstract—This paper deals with a well known puzzling observation that sometimes the wetting is improved by a chemical reaction between a liquid and a solid substrate and sometimes just the opposite effect takes place. Here, contact angles of liquid Al on SiO_2 and liquid Ti on Al_2O_3 have been measured. The surface and interface structures have been explored by scanning electron microscopy and energy dispersive X-ray spectrometry. According to the experimental observations, it turns out that the volume change of ceramic substrates during reaction plays a key role in the effect of chemical reaction on wetting. If the volume of ceramic substrate decreases after reaction, the wettability is not improved by the chemical reaction. This is the case of liquid Al wetting on SiO_2. If the volume of ceramic substrate increases after reaction, the wettability is improved by the chemical reaction. This is the case of liquid Ti wetting on Al_2O_3. Besides our experimental observations, results from literature have been reviewed as well, which are in good agreement with the predictions based on the volume change criterion of ceramic substrate proposed in this paper.

1. INTRODUCTION

The wetting phenomenon is of importance to the field of metal–ceramic engineering, such as in coating, joining and composite processing. However, most technologically meaningful ceramics are poorly wetted by non-reactive metals. In practice, wetting may be improved by adding other reactive elements, especially titanium additive. The beneficial effects of reactive additives on wettability have been addressed as due to two reasons: a reduction of interface energy contributed by the negative free energy of the chemical reaction between the reactive element and the substrate, and by the formation of a reaction product at the liquid–substrate interface.

Kritsalis *et al.* [1] studied the wetting of NiPd–Ti on Al_2O_3. The contact angle decreases with increasing titanium concentration. The composition analysis indicated that different reaction products have been formed at the interface when different concentrations of titanium were added. As the free energies of formation of these different reaction products are about the same, they concluded that the reduction of contact angle is due to the formation of different reaction products (titanium oxides) rather than by the negative free energies. Similar arguments have been put forward by various researchers for different systems: Li on Cu–Ti/Al_2O_3 [2] and Kalogeropoulou *et al.* on Fe/SiC [3]. However, they did not measure the contact angle of the liquid metals on the reaction products. The improvement of wetting due to the formation of reaction products at the interface is rather doubtful as the formation of a more stable ceramic compound during a chemical reaction would generally diminish wettability if at least an equilibrium state could be reached [4–6]. For instance, in the wetting of liquid Al on SiO_2 by Laurent *et al.* [7] and of liquid Al on CaO by Kucharski *et al.* [8], the chemical reactions contribute almost nothing to the wettability.

On the other hand, some experiments do indicate that wetting can be improved by a chemical reaction itself (negative Gibbs free energy of the reaction) rather than by the formation of a reaction product. A typical wetting experiment has been performed by Fujii *et al.* [9] in the wetting of liquid Al on BN and on AlN. The contact angle of liquid Al on BN at 1173 K reduces to 0°, where the reaction product at the interface is AlN. However, the contact angle of liquid Al on AlN in the same condition is much higher, i.e. 130°. Obviously, the reduction of contact angle of liquid Al on AlN is due to the chemical reaction itself instead of the formation of AlN at the interface.

Aksay *et al.* [6] have proposed a model combining a dynamic process of reaction and equilibrium state of wetting. According to their model, the contact angle would decrease first due to a chemical reaction, but then increases by a de-wetting process due to the formation of a more stable ceramic at interface. However, such an increment in contact angle has, to the best of our knowledge, never been observed

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Table 1. The experimental contact angles of liquid Al on SiO_2 and on Al_2O_3, and liquid Ti on Al_2O_3, as well as the relative volume change of ceramic after reaction $\Delta V/V_0$(%)

Metal	Ceramic	T (K)	θ_{exp} (deg)	Reaction product of ceramic	$\Delta V/V_0$ (%)
Al	SiO_2	1023	140 ± 5	Al_2O_3	−38
Al	SiO_2	1123	95 ± 5	Al_2O_3	−38
Al	SiO_2	1223	76 ± 5	Al_2O_3	−38
Al	Al_2O_3	1023	141 ± 5		
Al	Al_2O_3	1123	99 ± 2.5		
Al	Al_2O_3	1223	89 ± 2.2		
Ti	Al_2O_3	1973	42 ± 2	TiO_2, Ti_2O_3, TiO	+10, +22, +51

experimentally [1–3, 7–10]. In the treatment of reactive wetting, Aksay *et al.* [6] and Laurent *et al.* [7] attempted to introduce the negative free energy into the Young's equation of wetting. However, in principle the use of interface energy is valid only for an equilibrium state of wetting, but not for a dynamic situation like a reactive wetting, where rather the interface tension should be used which of course is not always equal to the interface energy. A more detailed discussion will be presented in Section 4.

In summary, the scientific literature is still confusing and rather puzzling about the effect of chemical reaction on wetting—sometimes, it is effective, but sometimes not. In other words, the mechanism of reactive wetting has not yet been established [11, 12]. This paper attempts to unravel the confusion by introducing the effects volume changes may have on wetting phenomena.

In this paper, two wetting experiments have been done of liquid Al on SiO_2 and of liquid Ti on Al_2O_3. According to the experimental results, a reactive wetting mechanism has been proposed, which can be successfully applied as well to the relevant results in literature.

2. EXPERIMENTS

The surface roughness of the Al_2O_3 substrate is about 0.01 μm and the wavelength is 5 μm measured by using a Stylus size of 5 μm. The phase of Al_2O_3 is α-Al_2O_3 as determined by X-ray diffraction. The wetting experiments of Al on SiO_2 (quartz glass) and on Al_2O_3 were done at 1023 K for 2 h, 1123 K for 2 h and at 1223 K for 1 h *in vacuo* of 10^{-4} Pa. The wetting experiment of Ti on Al_2O_3 was processed at about 1973 K for 5 min by Ar shielding. The contact angle was measured from the drop profile. Further, scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) have been applied to study the surface and interface structures between metals and ceramics.

3. EXPERIMENTAL RESULTS

Table 1 lists the measured contact angles. The contact angle of liquid Al on SiO_2 is about the same as that of liquid Al on Al_2O_3 at 1023 K, but much lower at higher temperature of 1223 K. The larger deviation in contact angles of liquid Al on SiO_2 is due to the non-spherical shape of the Al drop. The surface of the Al drop after reaction contains many Si precipitates as is illustrated in Fig. 1, which may prohibit the formation of a spherical shape of the liquid drop. The EDS composition analysis indicated that SiO_2 has been reacted with Al and transformed to Al_2O_3. The reacted surface of oxide shrank and became very rough after the reaction as is shown in Fig. 2. Many fine Si fibers have been formed on the reacted surface of substrate. In some cases, liquid Al was in contact only with the Si fibers (see Fig. 3). The cross-section of the reacted Al on SiO_2, as illustrated in Fig. 4, indicates that Al_2O_3 grains are largely separated by boundary cavities which are filled later by Al and Si. Many Si precipitates exist in the Al.

The contact angle of liquid Ti on Al_2O_3 is about 42°. Figure 5 shows the interface between Ti and

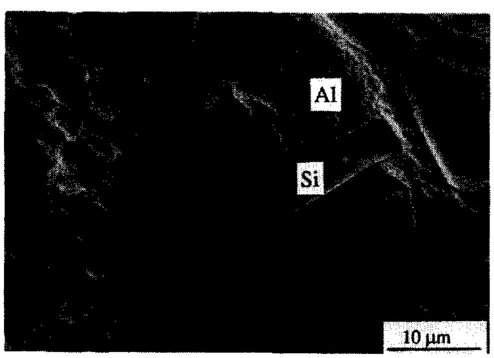

Fig. 1. The surface of the Al drop after reaction contains many Si precipitates, which may prohibit the formation of a spherical shape of the liquid drop.

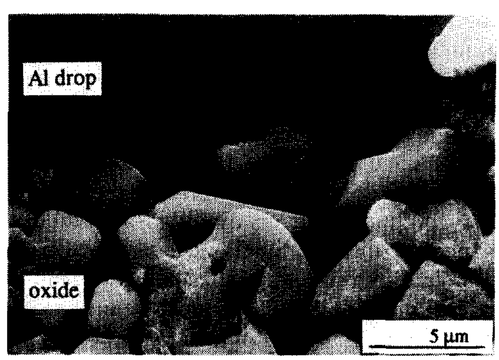

Fig. 2. The reacted surface of oxide shrank and became very rough afterwards. Many fine Si fibers have been formed on the reacted surface of substrate.

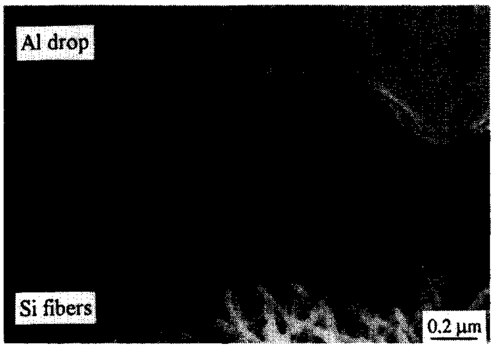

Fig. 3. The Si fibers formed on the Al_2O_3 surface provide a bridge connecting the liquid Al drop to the Al_2O_3 substrate.

Fig. 5. A cross-section of the interface between Ti and the Al_2O_3 showing that the reacted oxide Ti–Al–O was etched away by liquid Ti due to the low melting point of the oxide.

Al_2O_3. The EDS composition analysis indicated that a thin layer (of a few μm) of complex oxide Ti–Al–O has been formed at the interface. The concentration of Al in Ti varies between 5 and 10 at.%. As the melting point of the complex oxide is close to the experimental temperature according to the equilibrium phase diagram of Al_2O_3–TiO_2 [13], the complex oxide was etched away during reaction.

In Table 1, the relative volume change of ceramic after reaction are listed as well, where $(\Delta V/V_o)\% = [(V_r - V_o)/V_o]$ % and V_o and V_r represent the volumes of original and reacted ceramics, respectively.

4. DISCUSSION

In the wetting of liquid Al on SiO_2, the following chemical reaction occurred: $3SiO_2 + 4Al = 2Al_2O_3 + 3Si$. Herewith, the volume of the ceramic substrate was reduced by 38% from $3SiO_2$ to $2Al_2O_3$. As a consequence, the Al_2O_3 grains formed in the substrate were separated by cavities along the boundaries due to the volume shrinkage. Some of the liquid Al would diffuse easily into these cavities. In front of the wetting triple line, surface cavities may be induced due to the shrinkage of the ceramic substrate during the reaction as sketched in Fig. 6, which may hamper a further spreading of liquid drop over the surface.

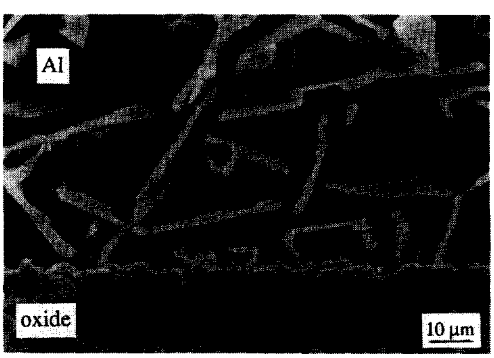

Fig. 4. The cross-section of Al drop on the reacted SiO_2 indicates that Al_2O_3 grains are separated by boundary cavities which may be filled later by Al and Si. Many Si precipitates exist in the Al drop.

Meanwhile, Al and Si may diffuse to the surface cavities through the boundary cavities of Al_2O_3 grains. Then a further reaction will occur in front of the triple line. In this way, the chemical reaction takes place on the surface of SiO_2 before the spreading of liquid Al drop. The wettability is predominated by the formation of Al_2O_3, but not by the Gibbs free energy contribution involved in the chemical reaction itself. In this case, the equilibrium contact angle θ_{eq} can be approximately written as

$$\cos\theta_{eq} = \frac{\sigma^r_{sv} - \sigma^r_{ls}}{\sigma_{lv}} \tag{1}$$

where σ_{lv}, σ^r_{sv} and σ^r_{ls} are the interface tensions of liquid metal–vapor, reacted ceramic–vapor and liquid metal–reacted ceramic–substrate, respectively. σ_{lv} may vary during reaction as the reaction product, like Si in this case, may diffuse into the liquid drop. According to equation (1), in the case of a reaction proceeding wetting, the wettability would not be improved by the chemical reaction, as the equilibrium contact angle between reacted ceramic and liquid metal is generally large.

The formation of the rough surface of Al_2O_3 and Si fibers on Al_2O_3 may have two effects on the wetting. Firstly, the wetting rate may be reduced significantly. Laurent *et al.* [7] have reported that the wetting time of Al on SiO_2 is rather long, of the order

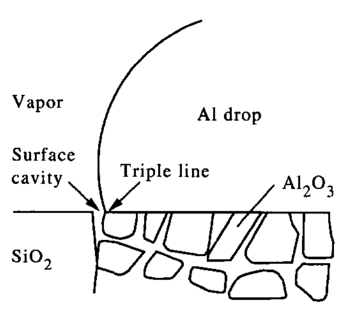

Fig. 6. A surface cavity is induced in front of the wetting triple line due to the shrinkage of the ceramic substrate after reaction. The surface cavity may hamper further spreading of the liquid drop.

of 1 h. Secondly, the real contact angle may greatly deviate from the equilibrium angle as described by equation (1). The contact angle may increase by increasing surface roughness if the angle is high, but decreases if the angle is low [14]. Consequently, the contact angle of Al on SiO_2 would be higher at lower temperature (with a higher contact angle), but lower at higher temperature (with a lower contact angle) compared to the angle of liquid Al on a smooth surface of Al_2O_3. Consequently, the contact angle of liquid Al on SiO_2 varies with temperature to a greater extent compared to that of liquid Al on Al_2O_3. The existence of Si fibers on the reacted substrate surface may also affect the contact angle, as Al is wetted much better by Si than by Al_2O_3.

In contrast to the reaction between SiO_2 and Al, the volume of solid ceramic increases by 10–51% in the reaction between Al_2O_3 and Ti, as listed in Table 1. As a result a dense layer of titanium aluminum oxide has been formed at the interface. It has been suggested [15] that the wetting process in metal–ceramic system is controlled by surface diffusion of liquid metal on ceramic substrate, where the driving force of surface diffusion is due to the difference of interface tensions (energies) between nonequilibrium state and equilibrium state. As surface diffusion is always faster than bulk diffusion, the chemical reaction would occur just at the wetting triple line as illustrated in Fig. 7(a). Consequently, the three interfaces at the triple line become metal–vapor, non-reacted ceramic–vapor and reactive metal–ceramic, where the interface tensions are σ_{lv}, σ_{sv} and $\sigma_{r\text{-}ls}$ respectively. As the reactive wetting is a dynamic process, the interface tension should be accounted for in the treatment rather than the interface energy. Here, the reactive metal–ceramic interface tension $\sigma_{r\text{-}ls}$ is not equal to Gibbs free energy (per unit area) of the

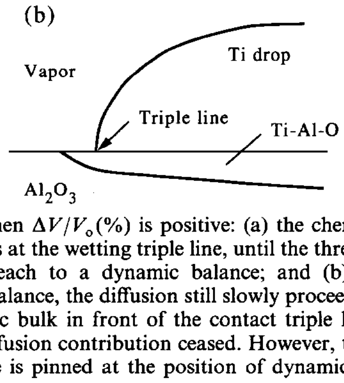

Fig. 7. When $\Delta V/V_o(\%)$ is positive: (a) the chemical reaction occurs at the wetting triple line, until the three interface tensions reach to a dynamic balance; and (b) after the dynamic balance, the diffusion still slowly proceeds through the ceramic bulk in front of the contact triple line, as the surface diffusion contribution ceased. However, the wetting triple line is pinned at the position of dynamic balance.

reaction. The following two arguments are proposed. First, only the horizontal component (on the surface) of the interatomic force (per unit length of triple line) contributes to the interface tension $\sigma_{r\text{-}ls}$. As the interatomic force is mostly in the perpendicular direction to the interface, the horizontal component is small. Secondly, the interatomic force is not correlated to the Gibbs free energy as an exchange of atoms is involved in a chemical reaction. In this sense, we suppose that the "effective" force from the reactive metal–ceramic interface acting on the liquid atoms at the wetting triple line does not contribute to the interface tension $\sigma_{r\text{-}ls}$, i.e. $\sigma_{r\text{-}ls} = 0$, which is independent of the value of Gibbs free energy of the chemical reaction. During the reactive wetting, the three interface tensions at the wetting triple line may reach a dynamic balance (i.e. different from an equilibrium state). Consequently, a balanced contact angle θ_{bal} would be achieved, where $\sigma_{r\text{-}ls} = 0$ is

$$\text{if } \sigma_{sv} \leqslant \sigma_{lv} \quad \cos\theta_{bal} = \frac{\sigma_{sv} - \sigma_{r\text{-}ls}}{\sigma_{lv}} = \frac{\sigma_{sv}}{\sigma_{lv}} \tag{2a}$$

and

$$\text{if } \sigma_{sv} > \sigma_{lv} \quad \cos\theta_{bal} = 1. \tag{2b}$$

Equation (2) indicates that a complete wetting ($\theta_{bal} = 0$) would be achieved only when the surface tension σ_{sv} of ceramic substrate is equal to, or larger than, the surface tension σ_{lv} of the liquid metal. Otherwise, a complete wetting would never be achieved in a reactive wetting. According to equation (2), not only the reactive elements in liquid metal may promote wetting, but also the non-reactive elements with a lower surface tension (in a reactive wetting system), as the elements with a lower surface tension may be segregated on the surface of liquid metals to reduce the surface tension. For instance, additives of inactive elements of Sn and In may improve the wetting of liquid Cu–Ti on Al_2O_3 [4] as the surface tensions of Sn ($\sigma_{Sn} = 0.537$ N/m) and In ($\sigma_{In} = 0.560$ N/m) are much lower than those of Cu ($\sigma_{Cu} = 1.27$ N/m) and Ti ($\sigma_{Ti} = 1.39$ N/m).

In the present wetting experiment of liquid Ti on Al_2O_3 at 1973 K, $\sigma_{Ti} = 1.39$ (N/m) [16], $\sigma_{Al2O3} = 0.98$ (N/m) [17–19], the balanced contact angle is calculated as $\theta_{bal} = 45°$, which is a little higher than the measured contact angle of 42°. The reason may be due to the effect of Al, as there is about 5–10 at.% of Al in Ti from the reaction. The surface tension of liquid Al at 1973 K is 0.719 (N/m), which may reduce the surface tension of the Ti liquid drop.

On the dynamic balance of three interface tensions, the surface diffusion ceases as the driving force for the surface diffusion becomes zero [15], but the bulk diffusion still slowly progresses further over the wetting triple line as illustrated in Fig. 7(b). However, the wetting would not process further as the contact angle on the dynamic balance represented by equation (2) is generally much smaller than the equilibrium contact angle given by equation (1). On the other hand, the wetting would also not move back (de-wetting), although $\theta_{eq} > \theta_{bal}$. In a separate paper [20], a rather novel phenomenon of wetting irreversibility has been observed in a non-reactive metal–ceramic system. According to those observations, de-wetting of liquid metal on ceramic does not occur, e.g. an equilibrium state could not be attained by means of de-wetting. Therefore, the contact angle on the dynamic balance would be preserved, although a more stable ceramic has been formed at the interface.

Summarizing our experimental results, it may be noticed that a criterion of ceramic volume change has been found in a reactive wetting: if the volume of ceramic substrate decreases after a chemical reaction, the wettability is not improved by the reaction; if the volume increases after reaction, the wettability is improved by the reaction.

As a possible support to the volume criterion of ceramic substrate in a reactive wetting, the available reactive wetting data from literature have been reviewed, which are listed in Table 2. Here, the relative volume change of ceramic substrate, the interface tensions and dynamic balanced contact angle have been calculated. If the volume of ceramic substrate increases after a chemical reaction, the wetting is improved by the reaction, otherwise it is not. In the case of pure liquid metals on ceramics, the balanced contact angles (where $\Delta V/V_o > 0$) are about the same as the measured angles. In the case of liquid metal containing reactive elements, the interface tension can be significantly reduced (where $\Delta V/V_o > 0$). As the content of reactive element in the liquid metal is insufficient, the non-reactive metal–ceramic interface may contribute to the wetting as well and the experimental contact angle would be larger than the calculated angle θ_{bal}.

In the calculation of Table 2, references of material properties should be taken with caution. The surface properties of ceramic may be different in different surrounding atmospheres. For instance, the surface of SiC is easily oxidized in an oxygen rich environment resulting in a thin layer of SiO_2 [21]. Consequently, the wetting behavior may be determined by the thin layer of SiO_2 rather than by the SiC bulk. The surface tension in a multicomponents liquid metal is mainly contributed by the element having the lowest surface tension if the content is large enough. The surface tension of liquid metal may also be influenced by the reaction product of metals in it.

Another point to bear in mind is that the Gibbs free energy is temperature dependent, which may change signs when increasing temperature. For instance, in the wetting of Fe on C, the chemical reaction does not occur at 1698 K ($\Delta G > 0$) [22], but it does at 1823 K ($\Delta G < 0$). Thus the wetting would be affected by reaction only at higher temperatures. The variation of $\Delta V/V_o(\%)$ in most reactive wetting

Table 2. Relative volume change of ceramic $\Delta V/V_o(\%)$, interface tensions and contact angles ("+" indicates that the wettability is improved by a chemical reaction, "−" is not improved)

Liquid metal	Ceramic substrate	Reaction product of ceramic	T (K)	$\Delta V/V_o$ (%)	Wetting	σ_{lv} (N/m)	σ_{sv} (N/m)	σ_{ls} (N/m)	θ_{exp} (deg.)	θ_{bal} (deg.)	Ref.
Al	AlN		1373			0.80	0.66	1.18	130		[9]
Al	BN	AlN	1373	+14	+	0.80	1.03	0	0	0	[9]
Al	Si_3N_4	AlN		+23	+						[4]
Al	10 nm-SiO_2/SiC	Al_2O_3	1073	−38	−	0.85	1.41	1.41	90		[7]
Al	15 nm-SiO_2/SiC	Al_2O_3	1173	−38	−	0.83	1.36	0.83	50		[7]
Al	SiC	Al_4C_3	1473	+30	+	0.79	2.50	0	0	0	[21]
AgCu	SiC		1223			0.92	2.33	3.04	140		[24]
AgCu–0.05Ti	SiC	TiC	1223	+0.01	+	0.92	1.19	0	0	>0	[24]
Cu	Al_2O_3		1350			1.35	1.27	2.27	138		[4]
Cu–0.095Ti	sapphire	Ti–O	1350	+10 ~ +51	+	1.35	1.43	0.26	30	>0	[2]
Cu–0.126Ti	sapphire	Ti–O	1350	+10 ~ +51	+	1.35	1.43	0.16	20	>0	[2]
Cu–0.126Ti	Al_2O_3	Ti–O	1350	+10 ~ +51	+	1.35	1.27	0.21	38	>20	[2]
NiPd	Al_2O_3		1523			1.50	1.19	1.50	102		[1]
NiPd–0.05Ti	Al_2O_3	Ti–O	1523	+10 ~ +51	+	1.50	1.19	1.37	97	>38	[1]
NiPd–0.15Ti	Al_2O_3	Ti–O	1523	+10 ~ +51	+	1.50	1.19	0.68	70	>38	[1]
NiPd–0.25Ti	Al_2O_3	Ti–O	1623	+10 ~ +51	+	1.50	1.14	0.23	50	>41	[1]
Cu	C		1350			1.35	1.90	2.99	144		[2]
Cu–12.6%Ti	C	TiC	1350	+128	+	1.35	1.90	0	0	0	[2]
Si	SiC		1753			0.74	2.19	1.59	36		[21]
Si	C	SiC	1723	+134	+	0.75	1.90	0	0	0	[23]
Fe	C		1698			1.82	1.90	0.99	60		[23]
Fe	C	Fe_3C	1823	+337	+	1.82	1.90	0	0	0	[23]
Fe	SiC	C	1633	−57	−	1.82	1.90	0.73	50		[3]
Fe–0.33%Si	SiC	C	1633	−57	−	0.75	1.90	1.29	35		[3]
Fe–0.66%Si	SiC	C	1633	−57	−	0.75	1.90	1.25	30		[3]
Al	Al_2O_3		1173			0.83	1.36	1.55	103		[8]
Al	SiO_2	Al_2O_3	973	−38	−	0.86	1.45	2.19	150		[8]
Al	SiO_2	Al_2O_3	1073	−38	−	0.85	1.41	1.53	98		[7]
Al	SiO_2	Al_2O_3	1173	−38	−	0.83	1.36	1.05	68		[7]
Al	CaO	Al_2O_3	1173	−50	−	0.83	1.36	1.5	100		[8]

is within 5% from room temperature to high temperatures. Therefore, the room temperature value could be used as an estimation, if $\Delta V/V_0(\%)$ differs greatly from zero. However, if $\Delta V/V_0(\%)$ is close to zero, high temperature values should be used. For instance, in the reaction of $Ti + SiC = TiC + Si$, the $\Delta V/V_0(\%)$ value is negative (-2.5%) at room temperature but positive ($+0.01\%$) at 1223 K.

In Table 2, the density of ceramic at room temperature and the surface tension of liquid metals are mostly taken from [16]. For the thermal expansion coefficient see Ref. [17]. The surface tension of ceramics are obtained from [21] for Si, from [23] for C, from [9] for BN and AlN, and combining from [17–19] for poly-Al_2O_3: $\sigma = 1.918 - 0.448 \times 10^{-3}T$ and for sapphire: $\sigma = 2.385 - 0.705 \times 10^{-3}T$ where the unit of the temperature T is in absolute temperature (K) and surface tension is in N/m. The temperature dependence of surface tension is usually not available for ceramics. The surface tension of Al_2O_3 varies greatly among the various papers. Although these uncertainties exist, the primary results of $\Delta V/V_0(\%)$, σ_{ls} and θ_{bal} in Table 2 would not change.

5. CONCLUSIONS

Contact angles in two different reactive systems of liquid Al on SiO_2 and liquid Ti on Al_2O_3 have been measured. The surface and interface structures have been studied by SEM and EDS. According to the experimental results, a criterion of ceramic volume change has been proposed in a reactive wetting of liquid metals on ceramic substrates. If the volume of ceramic decreases after a chemical reaction, surface cavities may be formed in front of the wetting triple line due to the volume shrinkage of the substrate. These surface cavities may hinder a further spreading of liquid drop. In the meantime, the chemical reaction may progress through the boundary cavities between reacted ceramic grains over the wetting triple line. Thus the wetting is predominated by the properties of reacted ceramic. Wettability would not be improved by the chemical reaction itself. In the opposite situation, if the volume of ceramic increases after reaction, a dense and thin layer of the reacted ceramic may be formed at the interface. Thus the reaction would occur at the contact triple line. The contact angle is given by a dynamic balance between three interface tensions at the triple line. The wettability can be improved significantly by the chemical reaction.

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